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LIQUID AND GAS PURIFICATION AND FILTRATION

The present invention relates to the removal of organic and other pollutants from liquids and gases, and in particular, but not exclusively, to the removal of such pollutants by a filtration system.

A number of strategies have been developed in the petrochemical industry for dealing with problems such as oil spillage and leakage, particularly at sea. Some methods, for example the use of detergents, simply aim to disperse the oil spillage as quickly as possible before too much damage has been done. It is, however, preferable to remove the oil from the water without allowing it to disperse, since there are many toxic components in the oil which may cause harm to the environment. It is known to provide a granular material based on cellulose, which has oil-absorbing properties, the material being in a form suitable for sprinkling onto an oil spillage. Once the oil has been absorbed, the material is gathered up and may be incinerated.

Oil spillages are not the only environmental problem faced by the petrochemical industry. There are many situations where it is desirable to remove components including organic pollutants (such as hydrocarbons) and heavy metal contaminants from produced water and water run-off before this water is released as effluent.

It is also desirable to remove such pollutants from liquids other than water and also from gases (e.g. air).

According to a first aspect of the present invention, there is provided a filter material comprising a matrix in which is dispersed a granular formulation of a material comprising a base formed

substantially of cellulose fibres onto which is adsorbed a composition comprising one or more aliphatic carboxylic acids having hydrocarbon chains consisting of 8 to 20 carbon atoms.

In preferred embodiments, the hydrocarbon chains of the one or more carboxylic acids consist of 10 to 18 carbon atoms. Particularly effective carboxylic acids have been found to include stearic acid $CH_3(CH_2)_{16}COOH$ and palmitic acid $CH_3(CH_2)_{14}COOH$.

According to a second aspect of the present invention, there is provided a method of producing a material comprising a base formed substantially of cellulose fibres onto which is adsorbed a composition comprising one or more aliphatic carboxylic acids having hydrocarbon chains consisting of 8 to 20 carbon atoms, wherein one or more cellulosic materials are mixed together with a powdered formulation of the one or more carboxylic acids.

The granular material of the first aspect of the present invention may be formed by mixing together one or more cellulosic materials, for example virgin pulp and wood chips, together with the one or more carboxylic acids in powder form and, optionally, latex. The mixing is preferably undertaken in a hammer mill, in which heat and friction assist the process whereby the carboxylic acid becomes adsorbed onto the cellulose fibres. It is thought that the carboxylic acids are adsorbed onto the surface of the cellulose fibres by way of the carboxyl -COOH functional group, either through hydrogen bonding or through the formation of cellulose esters containing an -O-CO-R group formed with the hydroxyl -OH groups on the cellulose rings. However the carboxylic acids are bonded to the cellulose fibres, the result is that the material of the first aspect of the present invention comprises cellulose fibres from which project hydrophobic

hydrocarbon chains. When the material is applied to a mixture of water and hydrocarbon pollutants, the hydrophobic hydrocarbon tails of the carboxylic acid residues serve to attract the hydrocarbon pollutants to the material and to repel water, thereby providing the required separation. The material, incorporating the hydrocarbon pollutants, can then be gathered up and used as a fuelstock.

The matrix of the first aspect of the invention may be fabricated from a number of materials, including non-woven fibrous materials, open-cell foam materials or a cotton or viscose gauze. The unloaded matrix advantageously has a density not greater than $0.25gcm^{-3}$, and preferably from 0.01 to $0.18gcm^{-3}$. A particularly preferred matrix has a thickness of around 3mm and a density in the region of $0.1gcm^{-3}$. The granular formulation of the material of the first aspect of the present invention may be incorporated into the matrix by bombardment across a pressure gradient as described in EP 0 504 214, the disclosure of which is hereby incorporated by reference into the present application. By incorporating the material of the first aspect of the present invention into a matrix to form a filter material, the available active surface area is increased so as to aid efficiency. Furthermore, dispersion of the material in the contaminated fluid is reduced because it is held within the matrix. In some embodiments, webs of the filter matrix are loaded to a density of around $1kgm^{-2}$; a density of $.925kgm^{-2}$ has been found to be particularly effective in certain circumstances. In other embodiments, a density of around $0.5kgm^{-2}$ has been found to be effective, particularly where the web of filter matrix has a thickness in the region of 3 or 4mm. Once

the filter material has become saturated with pollutants, it is relatively simple to remove the filter and replace it with a new one.

The filter material can carry over twice its own weight in hydrocarbons and is therefore useful as an energy source in, for example, cement kilns. In some situations, used filter material may be macerated into a form which can be fluidised and injected into furnaces as a fuelstock.

The filter material may be cut into shapes, such as discs, suitable for installation in filtration apparatus. Particularly preferred is a filter column comprising a hollow core upon which is mounted an alternating stack of filter plates and discs of the filter material of the third aspect of the present invention, wherein the filter plates are adapted to allow passage of fluid from a circumferential region of the filter column to the hollow core by way of the discs of filter material.

Alternatively, filter cartridges may be constructed by wrapping layers of the filter material around a central core. For example, a cylindrical cartridge may be made by taking a perforated tubular core, wrapping this with layers of filter material, providing a protective outer layer which allows passage of fluid into or out of the cartridge, and securing the whole with a pair of end caps. Fluid may be passed through the filter material in the cartridge either from the central core to the outside or from the outside to the central core.

One or more such filter cartridges may be advantageously installed in a filter pod comprising a casing internally divided into two chambers by a carrier which supports at least one filter cartridge, the carrier and the at least one cartridge being arranged so that fluid can only pass from one chamber

to the other by passing through both the hollow tubular core and the filter material of the at least one cartridge.

It is also possible to fill the aforementioned filter cartridges directly with the material of the first aspect of the present invention, without employing a filter matrix.

According to a fourth aspect of the present invention, there is provided a method of cleaning a fluid by contacting the fluid with a material comprising a base formed substantially of cellulose fibres onto which is adsorbed a composition comprising one or more aliphatic carboxylic acids having hydrocarbon chains consisting of 8 to 20 carbon atoms, wherein one or more cellulosic materials are mixed together with a powdered formulation of the one or more carboxylic acids.

Fluids which may be cleaned by this method include gases such as air, and liquids such as water. The material may be in loose form, such as a material according to the first aspect of the present invention, or the material may be bound in a matrix according to the third aspect of the present invention.

For a better understanding of the present invention and to show how it may be carried into effect, reference shall now be made, by way of example, to the accompanying drawings, in which:

FIGURE 1 shows a section through a yard-scale filter rig incorporating the material of the first aspect of the present invention;

FIGURE 2 is an exploded view of a filter column incorporating the filter material of the third aspect of the present invention;

FIGURE 3 shows a detail of a filter plate from Figure 2;

FIGURE 4 shows a test circuit including a filter

column similar to that of Figure 2;

FIGURE 5 shows a filter cartridge incorporating the filter material of the third aspect of the present invention;

FIGURE 6 shows a pod incorporating an array of the filter cartridges of Figure 5;

FIGURE 7 is a section through the pod of Figure 6;

FIGURE 8 shows a filter skid incorporating two of the pods of Figures 6 and 7;

FIGURE 9 shows a filter skid incorporating eight of the pods of Figures 6 and 7; and

FIGURE 10 is a graph showing the trends of flow/contamination data plotted against intervention periods for an eight-pod filter skid.

Initial small-scale trials:

There will firstly be described the results of small-scale laboratory analysis of a material according to the first aspect of the present invention. The differential pressure across columns of the material made from different types of cellulose was measured to gauge permeability and porosity characteristics of various substrates. The chosen grade showed no increase in differential pressure after 40 days flow. A particularly suitable grade of wood chip was found to be chips of a soft wood with a 30mm mean particle size.

Laboratory scale hydrocarbon filtration tests confirmed the oil-removing properties of the material. Two examples of the tests used follow:

Example 1: Dissolved hydrocarbons removed via column packed with 12g of material

575ml of Inde K condensate was added to 10 litres of artificial formation water (Brent recipe) and vigorously stirred using a homogeniser. Separate litre samples were then drained off, 100ml of each being

retained for triple peak analysis to measure the dissolved hydrocarbon content before filtration, and the remainder being added to a litre separation funnel mounted above the column. Triple peak analysis was carried out on the filtered water to provide before and after figures. Results are shown in table 1:

Table 1

Sample Litre	% Dissolved Hydrocarbons Removed
1st	86
2nd	72
3rd	83
4th	67
5th	82
6th	59
7th	75
8th	75

Example 2: Treatment of dry salt contaminated with hydrocarbons from a desalination plant

Batches of salt were rehydrated by adding 0.3kg of salt to 1 litre of pure water and passed through 12g of material at the rate of 1 litre/minute. The results are shown in tables 2 and 3.

Table 2

Hydrocarbons/ppm		
	Before	After
Sample 1	2826	2
Sample 2	4481	3

Table 3

Hydrocarbons/ppm				
	Before		After	
	Disp.	Diss.	Disp.	Diss.
Sample 3	1110	18	1	0
Sample 4	636	13	1	0

This small-scale analysis served to identify the physical nature of the substrate that retained permeability over long periods, absorbed high levels of hydrocarbons and was 100% incinerable. Accordingly, larger, yard scale trials could now commence:

Filtering trials through a yard scale filter:

Figure 1 shows a yard scale rig that is used in the following analysis. The rig comprises a pump (1) which pumps contaminated water via a flowmeter (2) to a diffuser (3) mounted over a filtration bed (4) provided with an amount of the material (5) according to the first aspect of the present invention. The filter bed (4) is located within a receptacle (6), from which the filtered water is passed via a sample valve (7) to a discharge (8).

Example 3:

Real produced water from Sean Papa platform was supplied and batches of 1000 litres were filtered through 0.5kg of material at 10 litres/minute. Samples were taken before each batch and samples of filtered water taken every 10 minutes. Typical results are set out in tables 4 and 5.

Table 4

Sample	Hydrocarbons/ppm		
	Dissolved	Total	% Reduction
Pre filter B	1870	26723	
Filtrate B1	20	338	98
Filtrate B2	15	453	98
Filtrate B3	11	432	99
Filtrate B4	10	381	99
Filtrate B5	7	367	99
Filtrate B6	8	374	99
Filtrate B7	6	354	99
Filtrate B8	2	341	99
Filtrate B9	6	432	98
Filtrate B10	1	314	99

Table 5

Sample	Hydrocarbons/ppm		
	Dissolved	Total	% Reduction
Pre filter D	211	1409	
Filtrate D1	9	28	98
Filtrate D2	5	27	98
Filtrate D3	4	25	99
Filtrate D4	3	28	99
Filtrate D5	4	27	99
Filtrate D6	4	28	99
Filtrate D7	2	27	99
Filtrate D8	2	28	99
Filtrate D9	2	27	98
Filtrate D10	1	26	99

In both these trials, the water had not been passed through any prefilter, coalescers or centrifuges, and therefore the total hydrocarbon levels (26723 - 1409ppm) were higher than expected. However, in a single pass through the filter, total hydrocarbon levels were reduced by an average >90%.

Specifically the dissolved fraction was reduced by an average 92%.

Typical suspended solids were 245ppm.

Formation of filter sheets:

There will now be discussed the use of the filter material of the third aspect of the present invention.

A granular formulation of a material according to a first aspect of the present invention is passed through a system that binds the loose product to, for example, a viscose or cotton gauze producing a 3mm thick mat that can be cut into shapes (typically discs) to fit existing filter hardware.

The process of forming such sheets increases the available surface area of the material thereby improving performance.

A prolonged programme of trials was undertaken to measure the performance of production grade discs in a commercially viable filtering system. The discs were installed in a filter column of the type shown in Figure 2, which comprises an alternating stack of filter plates (9) and discs (10) of filter material mounted on a hollow central core (12), the whole being compressed by an end plate (11) and placed in a suitable container (not shown). Figure 3 shows a filter plate (9) in more detail. Contaminated fluid is applied to the filter column such that it passes into the outside rim of each filter plate (9) and thence through an adjacent filter disc (10) before passing into the hollow central core (12) for extraction.

Example 4:

2000 litres of synthetic produced water with 22ppm suspended solids (median size 2.5 - 19µm) was filtered through a disc filter column of the type shown in Figure 2 loaded with 16 discs (10) of filter material, samples being taken before and after filtering. Two tests were run using two different flow rates, series I at 48 litres/minute and series II at 10 litres/minute, the results being presented in tables 6 and 7, with table 8 showing the analysis of the condensate supplied.

Table 6

Series I Hydrocarbon removal

48 litres/minute

		ppm			
		Dissolved	Dispersed	Total	Reduction
					%
	Pre filter	27	489	516	
Minutes	10	6	10	16	97
Minutes	15	5	17	22	96
Minutes	20	8	19	27	95
Minutes	25	8	34	42	92

Table 7

Series II Hydrocarbon removal

10 litres/minute

	ppm				
		Dissolved	Dispersed	Total	Reduct -ion
					%
	Pre filter	52	792	844	
Minutes	10	6	11	17	98
Minutes	15	13	15	28	97
Minutes	20	6	16	22	97
Minutes	25	6	15	21	98

Table 8:

Condensate Composition

Component	%age Weight
C1	<0.01
C2	0.04
C3	0.16
i-C4	0.17
n-C4	0.33
neo-C5	0.04
i-C5	0.37
n-C5	0.45
cyclo-C6	0.08
C6	1.99
Benzene	1.62

C7	3.55
Toluene	2.08
C8	3.70
Ethyl-benzene	0.53
Xylenes	3.42
C9	3.75
Isopropylbenzene	0.98
1,2,4 Trimethylbenzene	1.90
C10	6.65
C11	9.74
C12	8.90
C13	9.52
C14	8.96
C15	8.10
C16	5.23
C17	4.80
C18	3.54
C19	2.48
C20	1.78
C21	1.32
C22	0.98
C23	0.69
C24	0.60
C25	0.37
C26	0.34

C27	0.32
C28	0.26
C29	0.19
C30	0.07

In the following examples, the object was to establish the time taken for a given quantity of filter material discs to become saturated with hydrocarbons and to monitor continuously the hydrocarbon removal performance. These trials used fluorescing on-line hydrocarbon monitoring instruments.

Example 5:

A 16 disc filter using a prototype grade of material according to the first aspect of the present invention was used to treat 500ppm condensate in water. This was made up by homogenising the oil into a static water volume of 25 litres.

A laboratory fluorometer recorded:

Run 1 93.5% removal at 5 litres/minute
Run 2 96% removal at 5 litres/minute
Run 3 >87% removal at 5 litres/minute

Changes were made to the means of dispersing the oil in water as shown in the circuit of Figure 4, which comprises a contaminant dosing pump (13), a seven-stage homogenising pump (14), a filter column (15) and a sampling reservoir (16), wherein the sampling reservoir (16) generates an overflow stream and a monitored stream, the latter stream passing through an on-line monitor (17) adapted to detect the presence of hydrocarbons by fluorescence.

Production grade filter discs were manufactured for future tests to a repeatable commercial production formulation with a weight of $1000gm^{-2}$.

Example 6:

In this example, the filter column and discs used in Example 5 were reused. The 16 disc filter was connected on-line with a process monitor calibrated to the exact condensate type. The hydrocarbon-polluted stream was pumped through the 16 disc filter after dynamic mixing.

Contaminants were injected into the influent water at a constant rate through a positive displacement pump directly into the throat of the homogenising pump. The outlet pressure was controlled to 98psi. Samples for on-line analysis were taken directly through the falling stream cell; samples for laboratory analyses were taken before and after filtration.

For the first continuous test the metering of condensate was calibrated to 500ppm in water with a mean droplet size of <10μm. Over the next two hours the filter continued to remove >90% of the condensate in water supplied at a rate of 8 litres/minute. The test circuit shown in Figure 4 proved to be a satisfactory system for future trials to test efficiency and filter capacity.

Production grade filter discs were used in the following tests:

Example 7:

A nominal 300ppm condensate in water was passed at 4 litres/minute through a fresh filter column, the results being presented in table 9.

Table 9

Elapsed Time (h)	Through Filter (l/min)	Monitored Inlet Conc./ppm	Measured Outlet Conc./ppm	% Removal
0.00	4.02	312	16	95
2.50	4.05	305	18	94
3.75	4.05	310	20	94

Example 8:

This was a repeat of the 300ppm test at 4 litres/minute but using new filter discs. This test ran for seven hours before showing signs of reaching saturation, the results being presented in table 10.

Table 10

Elapsed Time (h)	Through Filter (l/min)	Monitored Inlet Conc./ppm	Measured Outlet Conc./ppm	% Removal
0.00	4.02	310		
1.00	4.02	307	6	98
1.50	4.00	295	6	98
2.25	3.97	312	8	97
3.25	4.00	312	10	97
4.25	4.00	308	12	96
5.25	4.05	310	13	96
7.00	3.98	312	18	94

Example 9:

A nominal 500ppm condensate was passed through the above filter stack at the same volumetric flow rate so as to accelerate saturation, the results being presented in table 11. The filter column is showing signs of failure.

Table 11

Elapsed Time (h)	Through Filter (l/min)	Monitored Inlet Conc./ppm	Measured Outlet Conc./ppm	% Removal
7.00	4.05	498	18	96
7.25	4.05	498	18	96
8.00	4.03	496	35	93
8.25	4.03	498	88	82

Example 10:

A nominal 500ppm condensate at 6 litres/minute was passed through the filter stack, the results being presented in table 12.

Table 12

Elapsed Time (h)	Through Filter (l/min)	Monitored Inlet Conc./ppm	Measured Outlet Conc./ppm	% Removal
0.00	6.51	515		
0.50	6.32	515	11	98
1.00	6.42	515	14	97
2.00	6.35	513	14	97
3.00	6.42	516	22	96
3.50	6.46	514	26	95
4.50	6.42	514	46	91
5.67	6.42	513	62	87

Example 11: Glycol removal

A larger filter housing using 18" filter discs was connected to the test rig shown in Figure 2. Glycol contaminated with hydrocarbons was supplied, this mixture was injected to the total stream of 14 litres/minute.

This level of contamination is beyond the

calibration range of the standard on-line monitor, but it was possible to use the 4-20mA output to monitor changes in the inlet flow to the filter.

Hand samples were taken for analysis before and after filtering. The results are shown in table 13.

Throughout the test the filters were operating at 17psi. The filter elements were on-line for 150 minutes.

Table 13

	ppm		%
	Prefilter	Post filter	Reduction
Glycol MEG	4520	797	82
Glycol MEG	4566	831	82
Dispersed hydrocarbons	95	0	100
Dissolved hydrocarbons	7	0	100

Example 12: Metals removal

In this example, water with the following levels of metals was used:

Nickel	1.75ppm
Copper	0.50ppm
Zinc	0.40ppm
Lead	0.30ppm

and the following was added to the water:

Condensate	0.5ppm
Leman silt	50ppm

Samples were taken before and after filtering, the results being shown in table 14. The increase in the metal content of the prefiltered water is ascribed to metals in the condensate and silt.

Table 14

	ppm		%
	Prefilter	Post filter	Reduction
Nickel	1.77	0.52	71
Copper	0.62	0.14	71
Zinc	2.9	0.25	57
Lead	0.42	<0.05	88

Formation of filter cartridges:

As an alternative to the disc filter column described above, a pod including one or more filter cartridges may be employed. As shown in Figure 5, a cartridge (18) is formed by wrapping filter material (19) around a tubular core (20) and applying a protective outer layer (21) and end caps (22). The protective outer layer (21) and the core (20) are provided with perforations (23,24) so as to allow passage of filtrate, either from the outside of the cartridge (18) through the filter material (19) to the inside of the core (20) or *vice versa*.

A typical cartridge (18) has a diameter of 215mm, a length of 1300mm and an internal diameter of 50mm, and is provided with 10.98kg of tightly-wrapped sheet filter material with a density of $0.925 kgm^{-2}$.

Example 13:

Figures 6 and 7 show a pod (25) in which an array of filter cartridges (18) is mounted on a carrier (26). The carrier (26) is adapted to allow filtrate ingressing from the bottom (27) of the pod (25) to pass only into the hollow cores (20) of the cartridges (18). The filtrate then passes through the filter material (19) and into the top (28) of the pod (25) (which is separated from the bottom (27) of the pod (25) by the carrier (26)), from where it exits the pod (25) by way of egress (29).

Example 14:

Figure 8 shows a filter skid (30) comprising two filter pods (25) and Figure 9 shows a filter skid (31) comprising eight filter pods (25). Figures 8 and 9 are not to scale. The pods (25) may be connected in series or in parallel in a number of configurations by way of alternative manifolding of the connecting pipework (32). A typical eight-pod skid (31) can accommodate flow rates of up to 120m^3/hour at working pressures of up to 4 bar.

Table 15 shows the results achieved for an eight-pod skid (31), each pod (25) comprising ten filter cartridges (18) and operated according to the following specifications:

Weight of filter material per cartridge: 10.98kg
Weight of filter material per vessel: 109.8kg
Weight of filter material in skip: 878.4kg
Oil contamination: 500mg/litre
Oil adsorption: 90%
MEG contamination: 500mg/litre
MEG adsorption: 80%
Flow: 1656 litres/hour

Table 15:

Flow litres/hour	Discharge			Retained contaminants		Interv-ention
Through filter	mg/l	kg/day	kg/annum	mg/l	kg/day	Days
1656	150	5.96	2176	850	33.79	52.00

Figure 10 shows a plot of the trends of flow rate against contamination and intervention periods for a typical eight-pod filter skid employing the filter material of the third aspect of the present invention.